On the Mechanism of Martensite Nucleation

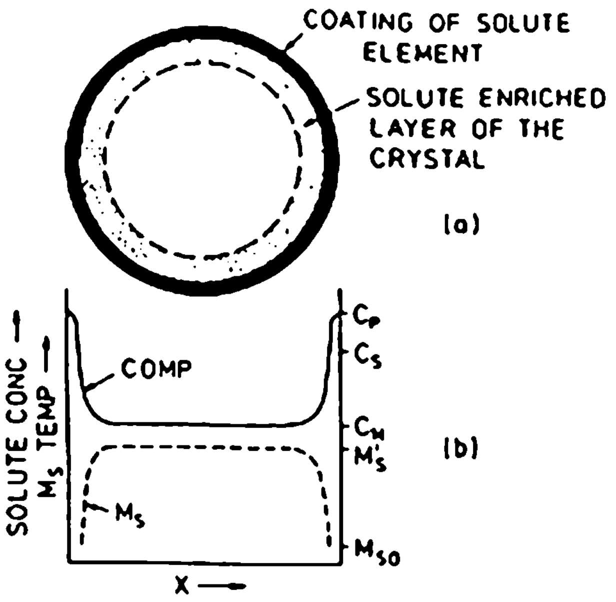
W. Krauss, Universitaet des Saarlandes, FB 12.1., Bau 2, D-6600 Saarbruecken, FRG
S.K. Pabi, Department of Metallurgical Engineering, Indian Institute of Technology, Kharagpur 721302, India
H. Gleiter, Universitaet des Saarlandes, FB 12.1., Bau 2, D-6600 Saarbruecken, FRG

Introduction

The martensitic transformation in the following two model systems, Fe-30 at.%Ni and In-5.25 at.%Cd, was studied by X-ray diffraction and metallography in order to answer the following questions: Does the nucleation of martensites occur by a soft mode mechanism or by classical heterogeneuous nucleation?

The experiments reported are based on the following idea. In Fe-Ni and In-Cd systems, the M temperatures decrease sharply with an increase of the Ni and/or the Cd content, respectively /1,2,3/. Hence, if small single crystals of an In-Cd or a Fe-Ni alloy with compositional gradients at their free surfaces are generated by coating and diffusion of Cd or Ni, respectively, into the microcrystals, the Cd- or Ni- enriched free surface region of the crystals would have a lower M_S temperature than the interior (Fig. 1). As a consequence, the particle surfaces cannot be effective nucleation sites unless the temperature approches the M_S temperature of the surfaces, M_{So}. Thus, the martensite nucleation process in the microcrystals remains the same irrespective of a composional gradient at the free surface, if the nucleation is predominantly homogeneous. However, if nucleation is heterogeneous, a comparison between the nucleation characteristics of small crystals with and without concentration gradients at their free surfaces would reveal the role of the free surface for the martensite nucleation process.

Fig. 1:



Schematic illustration of (a) the cross section through the Fe-Ni or In-Cd microcrystals coated with Ni or Cd followed by controlled diffusion to generate a solute enriched coherent surface layer and (b) the corresponding solute concentration C as well as the M_S temperatures. The C_P, C_S and C_M represent the concentrations in the coating, at the interface, between coating and crystal and inside of the microcrystal where solute enrichment has not occured. The corresponding M_S temperatures are M_{So} (at the free surface) and M'_S (in the center of the microcrystal). X is the distance measured from the center of the microcrystal.

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Experimental

About 100g of a Fe-30 at% Ni alloy (called alloy A) was prepared by melting 99.99% pure Fe and Ni in a high purity alumina crucible under a reducing atmosphere (~ 15% H). The alloy was remelted twice and homogenized at 1170 K for 2 days in the reducing atmosphere. The compositional homogeneity of the alloy was confirmed by elemental analysis in a scanning electron microscope.

An In-rich alloy containing 5.25 at% Cd (alloy B) was prepared from 99.999% pure In and Cd. The melt was throrougly shaken prior to solidification. The homogeneization was carried out in silicone oil at 390 K for about 4 days.

A polycrystalline powder of the alloy A was generated by filing. Single crystal spheres of the alloy A were produced by the 'drop-tube' technique /4,5/, where the filings were melted and solidified during free fall through a 3 m long quartz tube under protective atmosphere. The spheres were single crystals, 48μm-104μm in diameter, having the same Ni-content as the bulk. For studying the effect of particle size on the martensitic transformation in alloy A, the spheres were sieved in four groups, namely grade 1 with diameters ranging from 104 to 85μm, grade 2 with 84 to 75μm, grade 3 with 72 to 62μm and grade 4 with 61 to 48μm.

In order to produce single crystal spheres of alloy B, small droplets (diameter 30 to 45μm) were prepared by emulsifying /6/ the melt in oil. The droplets of the emulsion were cooled from 480 K to room temperature at a rate 10 K/h. The resulting spheres were washed repeatedly with water and acetone prior to drying at room temperature. Crystals larger than 45μm were discarded by sieving.

A portion of the spheres of alloy A of every grade was coated on all sides with pure (99.99%) Ni by sputtering. The thickness of the coating was 0.3μm. Some spheres of alloy B were completely coated (2-5μm) with Cd (99.999%) by vapour deposition. By subsequent annealing, the atoms of the coatings were diffused into a surface region of the crystals (Fig. 1). The concentration profile of the surface region was estimated /7/ from the diffusion data available in literature /8,9/. Usually, the width of the diffusion profile was too narrow to be measured in the scanning electron microscope. The diffusion/heat treatment for the alloy B was carried out in vacuum. The crystals of alloy A were sealed in quartz tubes filled with a protective atmosphere prior to the diffusion treatment. It is known /2,10/ that in Fe-30 at% Ni alloys martensite starts forming on cooling below 215 K. In order to initiate martensite formation in the coated specimens, cooling below ambient temperature was carried out in two ways: (i) by dipping the sealed quartz tube into liquid nitrogen and (ii) by means of a refrigerator cooling the spheres at a rate of 3 K± 0.5 K/min up to 78.7 K, thereafter the rate being 0.5 K/min to 16.5 K.

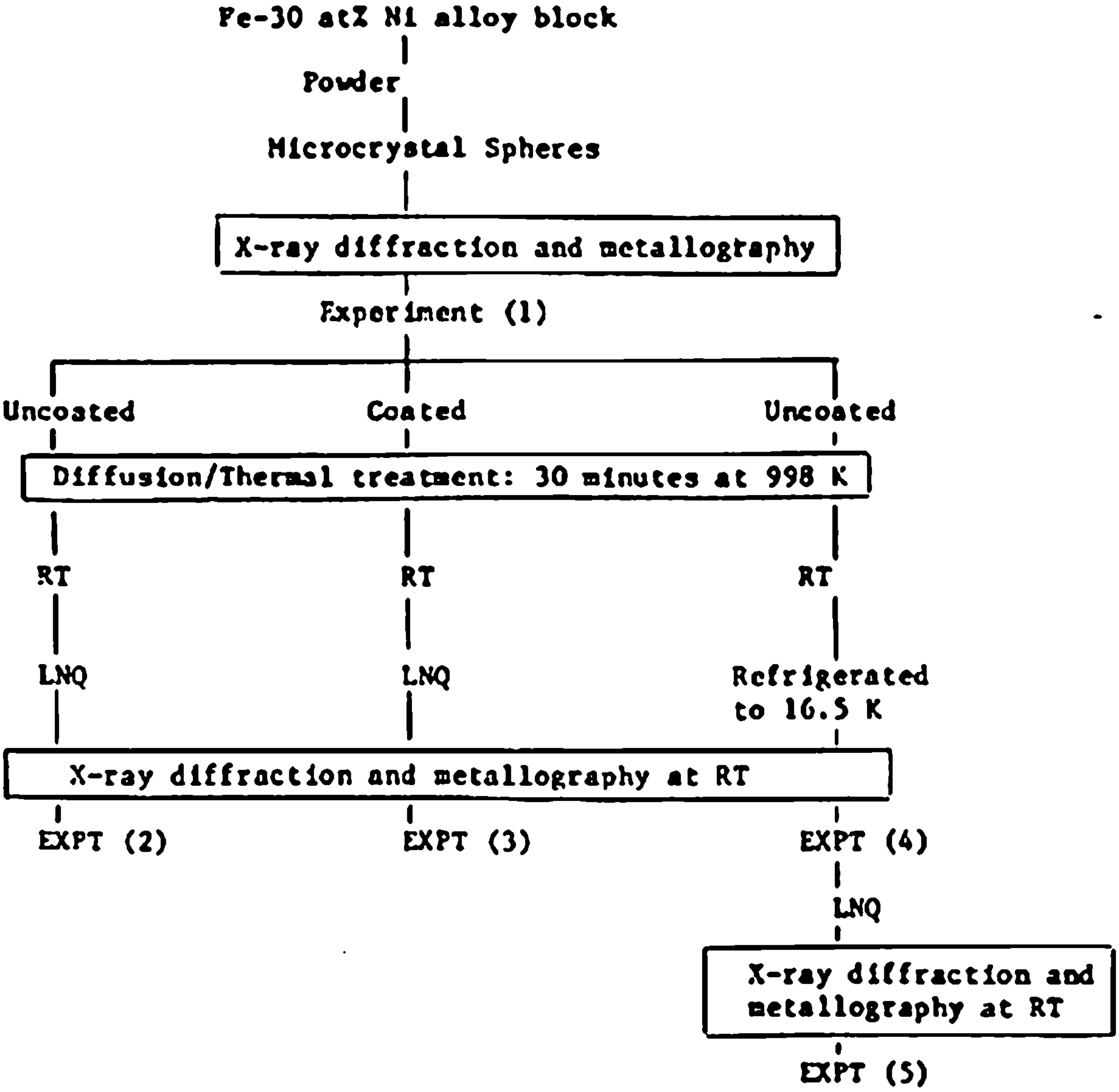
The martensitic transformation in all alloys was studied by X-ray diffraction with MoK_α radiation. The X-ray diffractometer stage used for alloy B was capable of controlling the temperature within ±0.2 K between 390 K and 140 K. Moreover, the room temperature was maintained at 298 K ± 1 K to prevent compositional changes in the specimen during the diffractometer alignment. Transformation in alloy A was also studied metallographically by mounting batches of 10 to 100 crystals in a cold setting resin.

Results

(a) Fe-Ni system

The program for the various experiments is displayed schematically in Fig. 2. The M_s , M_f , A_s and A_f temperatures of bulk Fe-30 at% Ni polycrystalline are /3,11,12/ 130 K, 215 K, 640 K and 670 K, respectively. This large transformation hysteresis allows all metallographic and X-ray examinations to be conducted at room temperature. The spheres obtained from the drop-tube had a fcc structure (cf. experiment 1, Fig. 2) with lattice parameter a=0.3578 nm.

Fig. 2: The scheme of experiments 1 through 5 with the Fe-Ni alloy. LNQ signifies liquid nitrogen-quenched; RT means room temperature and EXPT is the acronym for experiment.



On quenching the uncoated spheres to liquid nitrogen (cf. experiment 2), martensite formed with a lattice constant of a=0.2335 nm. These lattice parameters agree with the numbers quoted in literature /13,14/.

The percentage of martensite formed in experiments 2 to 5 are summarized in Table I. In experiments 2 and 3, the martensite formed during quenching in liquid nitrogen (LNQ). An increase of the sphere size had only limited influence No martensite formed in spheres coated on all sides with Ni (cf. Table I, experiment 3). The metallographic observations agreed with the X-ray diffraction data.

Table I: Percentage of martensite in Fe–30 at% Ni microcrystals measured in different experiments (cf. Fig. 2) by X-ray diffraction

Exp. No.	Surface Condition*	Type of Cooling**	Percentage martensite in different grades			
			grade 1	grade 2	grade 3	grade 4
				diameter		
			85-114 μm	73-74 μm	62-72 μm	48-61 μm
2	UC	LNQ	56	56	54	53.5
3	C	LNQ	0	0	0	0
4	UC	R, 16.5 K	0	0	-	-
5	UC	R, 16.5 K then LNQ	57	57.5	-	-

* UC = Uncoated, C = Coated
**LNQ = Liquid nitrogen quenched to 78.7 K; 'R, 16.5 K' signifies cooling in a refrigerator to 16.5 K

In experiment 4 (Fig. 2) the uncoated microcrystals were cooled slowly in a refrigerator to temperatures well below M_f. Metallography and X-ray diffraction revealed no martensite (Table I). At the end of experiment 4, the spheres were removed carefully from the X-ray diffractometer stage , washed thoroughly in acetone, dried, sealed in a quartz capsule and subsequently quenched in liquid nitrogen (Fig. 2, experiment 5). X-ray and metallographic studies revealed $\sim$57% martensite, which agrees with the results of the direct quench in liquid nitrogen (cf. Table I, experiments 2 and 5).

(b) In-Cd system
The small transformation hysteresis ($\sim$25 K) in this system /1,15/ precludes a metallographic study of the martensitic reaction. The results obtained from X-ray diffraction experiments may be summarized as follows.
1. Spheres of alloy B transform from fct to fcc structure at 338 K on heating, while on cooling the fct structure reverts at 313 K. These observations are in agreement with available data from bulk specimens /1/. Apparently, the small size of the microcrystals has not influenced the transformation characteristics.
2. Alloy B crystals coated with Cd and homogenized for 2 days at 298 K ± 0.1 K were fully fcc at 298 K. The crystals were homogenized for another 20 days and the fcc to fct transition was complete on cooling to 251 K. The equilibrium solubility /15/ of Cd in In at 298 K is 6.1 at%. For this composition, the phase transition should start at 280 K and complete at about 253 K /1/. In other words, Cd enrichment of the In rich matrix up to the equilibrium solubility limit (i.e. 6.1 at% at 298 K) seems to have taken place in coated microcrystals by diffusion from the Cd coating and any conceivable oxide layer on the In rich crystals did not impede the diffusion.

3. Alloy B coated with Cd and homogenized for 22 days at 298 K ± 0.1 K was heated for 30 minutes at 308 K and the temperature was brought down to 263 K at a rate of 15 K/min; thereafter the cooling rate was slowed down to about 1 K/min. The martensite structure appeared at 250 K and the reaction seems to be complete at 233 K. The diffusion treatment at 308 K would bring down the M_{50} to 130 K /1,15/ making the surface region of the spheres ineffective for martensite nucleation at 233 K.

Conclusions

1. Nucleation of martensite in Fe-30 at% Ni microcrystals is heterogeneous. Surfaces have great potency as nucleation sites. Other lattice defects (dislocations, vacancies) seem to have less pronounced influence on the nucleation frequency.
2. Martensite formation in Fe-30 at% Ni microcrystals is completely suppressed by slow cooling. Possibly quenching stresses play an important role in the nucleation of ferrous martensites.
3. 'Soft mode nucleation' or 'localized soft mode nucleation' theories seem at variance with the observed nucleation characteristics of martensite in Fe-Ni alloys.
4. Surface and lattice dislocations have little influence in the diffusionless fcc → fct transition of In-Cd alloys. The nucleation process here is predominantly homogeneous, which may be explained by the soft-mode nucleation theory.
5. Lattice softening may not in all systems be crucial for the martensitic nucleation process.

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